Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; mol. wt., 188. Found: C, 89.37; H, 10.71; mol. wt., 190.

The infrared and n.m.r. spectra of the photodimer **4** were identical with the corresponding spectra of the hydrogenation product of **1** to the smallest detail.

Photosensitized Dimerization of Norbornene. A solution of norbornene (320 g., 3.41 moles), acetophenone (41 g., 0.34 mole), and benzene (150 ml.) was charged to the reactor previously described. A Pyrex immersion finger replaced the Vycor finger containing the mercury arc. Irradiation was carried out for 192 hr. with continuous nitrogen ebullition. The reaction temperature was maintained at 29 ± 2°. After the irradiation was completed, the benzene, acetophenone, and unreacted norbornene were removed by distillation. The residual liquid, analyzed by v.p.c.,[32] contained dimers **4** and **6** in a 12:88 ratio, in addition to small amounts of higher boiling products. Careful fractionation on an 18-in. spinning-band column afforded 11 cuts of dimer (boiling range 92–110° at 3 mm., 72.2 g., 0.768 mole, 23% yield). The fraction boiling at 100–102° at 1 mm. was shown to be pure **6** by v.p.c. analysis.[32] This fraction crystallized upon standing to give clear plates that melted at 38.5–39.5°.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; mol. wt., 188. Found: C, 89.57; H, 10.51; mol. wt., 191.

The mixture melting point of **6** with the hydrogenation product of **3** was undepressed (38–39°). The infrared and n.m.r. spectra of the two were identical.

Catalytic Reduction of Norbornadiene. A solution of norbornadiene (2.30 g., 0.025 mole) in benzene (50 ml.) to which palladium on carbon (5%, 0.1 g.) had been added was stirred under a deuterium atmosphere. The reaction was stopped when the uptake of deuterium was equivalent to 1.1 moles. The solution was filtered from the catalyst and brought back to the original volume by the addition of benzene. Analysis by v.p.c. showed only a trace of norbornadiene remaining with dideuterionorbornene equivalent to a 63% yield, the rest being tetradeuterionorbornane. This solution was used in the acetophenone-sensitized dimerization without further purification. In the case of the cuprous chloride catalyzed dimerization ether replaced benzene as the solvent for reduction. Pure samples of dideuterionorbornene and tetradeuterionorbornane for n.m.r. were obtained by preparative-scale gas chromotography.[36]

N.m.r. Spectra. N.m.r. spectra were measured on a Varian A-60 spectrometer operating in a V-4012-SM 12-in. magnet gap. The heteronuclear double resonance experiments were conducted using an HR-60 spectrometer and an NMR Specialties HD-60 spin decoupler. Homonuclear field-sweep decoupling experiments were carried out by addition of a 1200-c.p.s. audio side-band detector similar to that described by Johnson.[37] A somewhat similar unit with an added 2-kc. tuning fork oscillator served as a field-frequency locking system in the manner described by Primas,[38] and Freeman and Anderson.[39] For frequency-swept experiments the 1200-c.p.s. oscillator driving the first side-band detector was replaced with a General Radio Type 1107-A interpolation oscillator modified for motor drive.

(36) Wilkens A-700 Autoprep silicon oil SE-30 (30%) on Chromosorb P column (20 ft.), 100°, helium gas.

(37) L. F. Johnson in "NMR and EPR Spectroscopy," Varian Associates Staff and Consultants, Pergamon Press, Inc., New York, N. Y., 1960, p. 187.

(38) H. Primas, Fifth European Congress on Molecular Spectroscopy, Amsterdam, 1961.

(39) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

Oxidative Cleavage of Cyclopropanes. III.[1,2] The Stereochemistry and Direction of Cleavage of Bicyclo[*n*.1.0]alkanes by Lead Tetraacetate and Thallium Triacetate

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The direction and stereochemistry of the oxidative cleavage of the cyclopropane bond by lead tetraacetate and thallium triacetate has been determined by utilizing bicyclo[4.1.0]heptane, bicyclo[3.1.0]hexane, and bicyclo[2.1.0]pentane. The facility of bond cleavage increases as the strain of the system increases. Products resulting from internal bond cleavage increase with decreasing ring size. External bond cleavage yields exclusively trans-2-acetoxymethylcycloalkyl acetates. Internal bond cleavage results in the formation of unsaturated monoacetates and 1,3-diacetates. The stereochemistry of the diacetates that result from internal bond cleavage is a function of the mode of decomposition of the intermediate organometallic derivative. Oxidative cleavage of cyclopropanes is postulated to occur via a two-step process in which electrophilic attack of the metal salt results in the formation of an organometallic derivative, which then solvolytically decomposes. The apparent rate of electrophilic attack of lead tetraacetate is slower than that of thallium triacetate, while the rate of decomposition of the organolead intermediate is faster than that of the organothallium intermediate.

(1) Part I: R. J. Ouellette and D. L. Shaw, *J. Am. Chem. Soc.*, **86**, 1651 (1964); part II: R. J. Ouellette, D. L. Shaw, and A. South, Jr., *ibid.*, **86**, 2744 (1964).

(2) Initial research was carried out with partial support of a Petroleum Research Fund Starter Grant. This research was also supported by Grant-GP 3873 from The National Science Foundation.

Introduction

The cleavage of carbon–carbon bonds in cyclopropanes by electrophilic reagents with the formation of products that result from addition of the reagent has been known since the 19th century.[3] The ring cleavage process can be interpreted on the basis of initial electrophilic attack to yield an intermediate of carbonium ion like character followed by neutralization of charge by a nucleophile. The direction of cleavage is therefore a reflection of the stability of the carbonium ion.[4] Early investigations have dealt with the problem of the position of ring cleavage as a function of substitution.[5] Only recently has the question of stereochemistry been examined.[6]

In a detailed study of the acid-catalyzed addition of acetic acid to bicyclo[*n*.1.0]alkanes, LaLonde[6b] observed products resulting from both internal and external bond cleavage. The extent of internal bond cleavage was found to increase with the strain of the compound. Addition of acetic acid to the external bond of bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane does not occur with complete stereospecificity, but a large predominance of *trans* products was observed. In the systems reported, the stereochemistry of internal bond cleavage could not be ascertained. More recently, LaLonde[6e] has found that internal bond cleavage of *exo*-7-methylbicyclo[4.1.0]heptane and *exo*-6-methylbicyclo[3.1.0]hexane also results in predominantly *trans* products.

While the extrapolation of LaLonde's observations to the cleavage of cyclopropanes by other electrophiles and a comparison of cyclopropane cleavage with that of polar addition to double bonds is tempting, it probably should be done with caution. The well-accepted principle of *trans* additions to alkenes has been reinvestigated recently, and *cis* addition has been found to occur in certain systems.[7] Of particular significance with respect to the use of metal salts as electrophiles, is the observation that mercuric salts add *cis* to certain alkenes.[8]

In two previous communications, we reported that the reaction of lead tetraacetate and thallium triacetate with cyclopropanes is general for alkyl- and aryl-substituted cyclopropanes. The stereospecificity of the reaction was indicated by the formation of *trans*-2-acetoxymethylcyclohexyl acetate without the corresponding *cis* isomer.

Levina reported the cleavage of bicyclo[4.1.0]heptane, bicyclo[3.1.0]hexane, and bicyclo[2.1.0]pentane by mercuric acetate.[9] Only the yields of the organomercury products were given, and these were less than quantitative. The rate of solvolysis of organomercury compounds is known to be extremely sensitive to changes in structure[10] and preferential decomposition of the organomercury compound would drastically affect the experimental results and their interpretation.

Criegee[6a] reported that bicyclo[2.1.0]pentane is cleaved by lead tetraacetate to yield *cis*-1,3-diacetoxycyclopentane. An unidentified lower boiling product was also obtained. Prior to our communication, this was the only reported case of cyclopropane cleavage by lead tetraacetate. Bicyclo[2.1.0]pentane is an extremely reactive compound and, therefore, the generality of the reaction was not established. We felt that the *cis* structure was either the result of a change in mechanism from the more usual *trans* addition noted in other compounds investigated in this laboratory or that the reported stereochemistry was incorrect. In this paper, this question will be resolved.

After our initial reports in which the stereospecificity of the cleavage of bicyclo[4.1.0]heptane by lead tetraacetate and thallium triacetate was established, Moon[6g] presented a partial study of the cleavage of bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane by lead tetraacetate.

In order to clarify the general reaction of oxidative cleavage of cyclopropanes, we report the cleavage of bicyclo[4.1.0]heptane, bicyclo[3.1.0]hexane, and bicyclo[2.1.0]pentane by both lead tetraacetate and thallium triacetate.

Results

The reaction of a 1.0 *M* solution of bicyclo[4.1.0]heptane with 0.5 *M* lead tetraacetate in acetic acid occurs quantitatively at 75° in 60 hr. Addition of water to the reaction mixture indicated that all lead tetraacetate had been transformed to lead diacetate as evidenced by the absence of a brown lead oxide precipitate. The remaining bicyclo[4.1.0]heptane and products were accounted for by gas chromatography. Analysis of the reaction mixture was accomplished by using a 10 ft. × 1/8 in. 20% Carbowax 20M on 60–80 Chromosorb W column at 180°. The reaction mixture consisted of 76.7% isomeric diacetates and 23.3% unsaturated monoacetates. The diacetate fraction was separated into two components. The major peak, which was 69.2% of the total reaction product, had the same retention time as the two isomeric 2-acetoxymethylcyclohexyl acetates. Collection of the material from the v.p.c. column and analysis by n.m.r. indicated that only *trans*-2-acetoxymethylcyclohexyl acetate was present. A sharp singlet at τ 8.10 corresponding to six hydrogens is observed for the two acetate methyl groups in the *trans* isomer. The *cis* isomer has two sharp singlets at τ 8.10 and 8.03 each of which corresponds to three hydrogens. The *cis* isomer could be detected if it were present to the extent of 1% of the

(3) (a) A. Baeyer, *Chem. Ber.*, **18**, 2277 (1885); (b) R. Fittig and F. Roder, *Ann.*, **227**, 13 (1885); (c) G. Gustavson, *J. prakt. Chem.*, [2] **36**, 300 (1887).

(4) (a) R. A. Raphael, "Chemistry of Carbon Compounds," Vol. II, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1953, p. 26; (b) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1954, Chapter 3.

(5) For reviews see (a) R. Breslow, "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 4; (b) P. deMayo, *Perfumery Essent. Oil Record*, **49**, 238 (1958); (c) M. Yu. LuKina, *Usp. Khim.*, **31**, 901 (1962).

(6) (a) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957); (b) R. T. LaLonde and L. S. Ferney, *J. Am. Chem. Soc.*, **85**, 3767 (1963); (c) R. T. LaLonde and M. A. Tobias, *ibid.*, **85**, 3771 (1963); (d) R. C. Cookson, D. P. G. Hamon, and J. Hudec, *J. Chem. Soc.*, 5782 (1963); (e) R. T. LaLonde and M. A. Tobias, *J. Am. Chem. Soc.*, **86**, 4068 (1964); (f) A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964); (g) S. Moon, *J. Org. Chem.*, **29**, 3456 (1964).

(7) (a) I. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962); (b) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2248, 3645 (1963); (c) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963); (d) H. Kuart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964).

(8) (a) T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, **No. 19**, 15 (1959); (b) M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1961); (c) T. C. Taylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); (d) T. G. Traylor and J. Traylor, *ibid.*, **86**, 244 (1964).

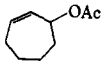
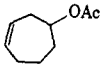
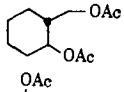
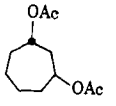
(9) R. Ya. Levina, B. N. Kostin, and T. K. Ustynyuk, *Zh. Obshch. Khim.*, **30**, 359 (1960).

(10) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4478 (1961).

diacetate fraction.[11] A small peak which corresponded to 7.5% of the reaction mixture was observed at longer retention time than that of *trans*-2-acetoxymethylcyclohexyl acetate. This peak had the same retention time as that of *trans*-1,3-diacetoxycycloheptane. The isomeric *cis* compound had a different retention time than any of the compounds of the diacetate fraction and could have been detected if it were present to the extent of 0.5% of the reaction product. In order to resolve the unsaturated monoacetate fraction, the temperature of the v.p.c. column was lowered to 115°. Two peaks whose retention times corresponded to Δ^2-cycloheptenyl acetate and Δ^3-cycloheptenyl acetate were observed. The yields of the two isomeric unsaturated monoacetates were 8.9 and 11.5%, respectively. A third peak corresponding to 2.9% of the reaction product was unidentified.

The cleavage of bicyclo[4.1.0]heptane by thallium triacetate in acetic acid occurs rapidly at 75°. Approximately 1 hr. is required for the reaction as indicated by monitoring the v.p.c. peak of the starting material. However, it is necessary to allow the reaction to proceed for an additional 82 hr. to ensure complete decomposition of the organothallium intermediate. Analysis of the reaction mixture was carried out utilizing the same techniques described for the lead tetraacetate cleavage. The reaction mixture consisted of 3.0% Δ^3-cycloheptenyl acetate, 91.0% *trans*-2-acetoxymethylcyclohexyl acetate, and 6.0% *trans*-1,3-diacetoxycycloheptane. The yields of both the lead tetraacetate and thallium triacetate cleavage products are given in Table I.

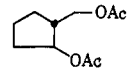
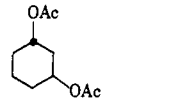
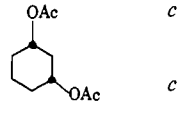
Table I. Cleavage Products from Bicyclo[4.1.0]heptane

Product		Yield, % $Pb(OAc)_4$	Yield, % $Tl(OAc)_3$
	*a*	8.9	Trace
	*b*	11.5	3.0
	*c*	69.2	91.0
	*d*	7.5	6.0

[a] A. C. Cope, T. A., Liss, and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 6287 (1957). [b] A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4843 (1962). [c] L. L. Colby, C. N. Lieske, D. R. Rosencrantz, and M. J. Schwarz, *ibid.*, **85**, 47 (1963). [d] A. C. Cope, J. K. Heeren, and V. Seeman, *J. Org. Chem.*, **28**, 516 (1963).

Bicyclo[3.1.0]hexane reacts with both lead tetracetate and thallium triacetate at 75° but at a somewhat faster rate. The diacetate fraction constituted 49.0% of the reaction mixture with lead tetraacetate and 55.5% with thallium triacetate. Unsaturated monoacetates accounted for the remainder of the product in each case. The diacetate fraction was readily resolved on a Carbowax 20M column at 165°. The fraction consisted of three components which had the same retention times as *trans*-2-acetoxymethylcyclopentyl acetate, *trans*-1,3-diacetoxycyclohexane, and *cis*-1,3-diacetoxycyclohexane. It was necessary to identify the *trans*-2-acetoxymethylcyclopentyl acetate by n.m.r. as the *cis* isomer had the identical retention time. The methylene hydrogens on the carbon bearing the acetoxy group in the *cis* isomer appear as the AB portion of an ABX spectrum in which four of the eight possible lines are intense. The center of mass of the multiplet occurs at τ 6.05. The spectrum of the *trans* isomer is considerably simpler and only two of the eight possible lines are intense. The center of mass of the signals occurs at τ 6.00. The spectrum of the collected reaction product was identical with that of *trans*-2-acetoxymethylcyclopentyl acetate. Analysis of the unsaturated monoacetate fraction was accomplished by v.p.c. Two peaks corresponding to Δ^2-cyclohexenyl acetate and Δ^3-cyclohexenyl acetate were observed. The yields of all products obtained with lead tetraacetate and thallium triacetate are given in Table II.

Table II. Cleavage Products of Bicyclo[3.1.0]hexane

Product		Yield, % $Pb(OAc)_4$	Yield, % $Tl(OAc)_3$
	a	24.0	19.6
	b	27.0	24.9
		24.5	46.5
		Trace	3.4
	*c*	24.5	5.6

[a] Yu. A. Arbuzov and T. A. Mastrgukova, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 665 (1952). [b] C. J. Gogek, R. Y. Mair, J. A. McRae, and C. B. Purves, *Can. J. Chem.*, **29**, 938 (1951). [c] W. Rigby, *J. Chem. Soc.*, 1586 (1949).

Bicyclo[2.1.0]pentane[12] reacts with lead tetraacetate and thallium triacetate at 25° to give Δ^2-cyclopentenyl acetate, Δ^3-cyclopentenyl acetate, and *trans*-1,3-diacetoxycyclopentane. The products were identified by v.p.c. The *cis* isomer was shown to be absent. The yields of each product are given in Table III.

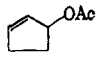
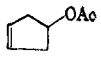
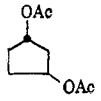
Discussion

The cleavage of cyclopropane bonds by electrophiles such as acids and metal salts occurs between the least substituted and most substituted carbon atoms unless factors other than electronic are operative. Polarization of the cyclopropane bond under the influence of a perturbing electrophilic reagent serves as an adequate model to explain the direction of bond cleavage. In a transition state in which polarization of the cyclopropane bond occurs, a partial negative charge would be best accommodated on a primary carbon, whereas a

(11) The authors are indebted to Dr. Lloyd Dolby for authentic samples of *cis*- and *trans*-2-acetoxymethylcyclohexyl acetate.

(12) The authors wish to thank Dr. Paul Gassman and Mr. Kevin Mansfield for the bicyclo[2.1.0]pentane used in this study.

Table III. Cleavage Products of Bicyclo[2.1.0]pentane

Product		Yield, % $Pb(OAc)_4$	Yield, % $Tl(OAc)_3$
	*a*	24.8	22.5
	*b*	35.7	27.5
	*c*	39.5	50.0

[a] K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956). [b] E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960). [c] L. N. Owen and O. N. Smith, *J. Chem. Soc.*, 4055 (1952).

positive charge would tend to be located on a substituted carbon atom.

In the bicyclo[*n*.1.0]alkanes, external bond cleavage would be expected to predominate over internal cleavage both on the basis of favorable energetics and a statistical factor of 2. Furthermore, there is less steric hindrance to approach by a reagent at an external bond as compared to an internal bond. However, relief of strain by cleavage of the internal bond should lead to a lowering of the transition state relative to external bond cleavage. The expectation that internal bond cleavage products should increase with decreasing ring size has been experimentally verified by LaLonde in the acid cleavage of cyclopropanes. We observe a similar trend with lead tetraacetate and thallium triacetate. The ratios of external to internal bond cleavage for the three bicyclo[*n*.1.0]-alkanes investigated in this study are given in Table IV with those of LaLonde[6b] for the acid cleavage reaction. The high reactivity of the internal bond of bicyclo-[2.1.0]pentane leads to exclusive internal cleavage for all three electrophiles and does not provide any information regarding the selectivity of the reagents. The bicyclo[4.1.0]heptane system is cleaved at both possible bonds with the external bond cleavage predominating in all three cases. The acid cleavage exhibits high selectivity indicating that charge is well developed in the transition state which leads to a large difference in the relative energies of the two possible states. With lead tetraacetate the selectivity is less for both bicyclo[4.1.0]heptane and bicyclo[3.1.0]-hexane systems, which probably indicates that the transition state lies closer to starting material with the development of less charge than for the acid cleavage.

Table IV. External to Internal Bond Cleavage Ratios for Electrophilic Attack on Bicyclo[*n*.1.0]alkanes

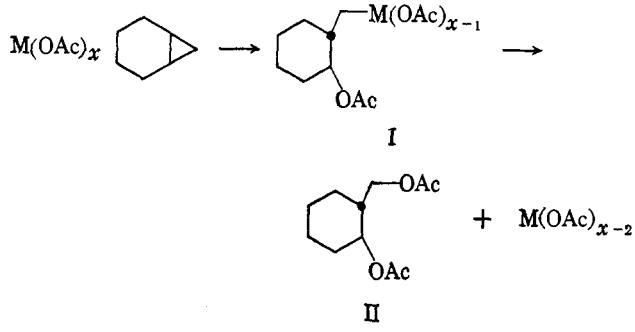
n	Proton[a]	$Pb(OAc)_4$[b]	$Tl(OAc)_3$[b]
4	11	2.1	10.1
3	4	0.3	0.9
2	0	0	0

[a] Taken from ref. 6b. [b] Calculated from the data in Tables I, II, and III.

Thallium triacetate is considerably more selective than lead tetraacetate.[13] The selectivity of the metal salts drops dramatically from the bicyclo[4.1.0]heptane to the bicyclo[3.1.0]hexane system. This decrease in selectivity indicates that the transition state leading to cleavage by metal salts is strongly dependent on the strain of the bicyclic system. With a proton acting as the electrophile, strain factors apparently are slow to overcome the electronic factor. However, with metal salts, where the charge development in the transition state is less, the strain factor becomes more important.

The stereochemistry of the cleavage of both internal and external bonds can be rationalized in terms of a *trans* addition mechanism for all bicyclo[*n*.1.0]alkanes investigated. The stereochemistry of the ultimate product, however, is dependent on the mode of decomposition of the intermediate organometallic compound. In the following discussion of the cleavage and solvolytic step, the symbols $M(OAc)_x$ will be used to represent both lead tetraacetate and thallium triacetate.

Cleavage of the external bond of bicyclo[4.1.0]heptane by $M(OAc)_x$ occurs stereospecifically to yield exclusively *trans*-2-acetoxymethylcyclohexyl acetate (II) as the stereochemistry of the ultimate product is unaffected in the solvolytic step. The intermediate organometallic I must, therefore, result from a closely timed sequence in which the addition of metal salt and solvent occur in such a fashion as to preclude loss of stereochemistry. The organomercury compound derived from external bond cleavage of bicyclo[4.1.0]heptane has been isolated by Levina and shown to be *trans*.[9]



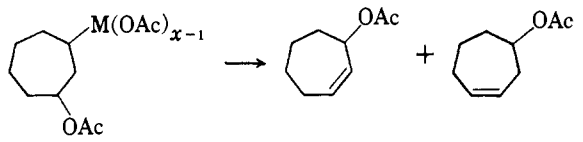
Apparently very little charge is developed at the secondary ring carbon when the solvent attacks as indicated by the decreased selectivity compared to the acid cleavage. The intermediate organometallic compound does not yield any unsaturated material in contrast to secondary organometallic compounds to be described below.[14]

Internal bond cleavage should also yield an organometallic intermediate of *trans* configuration (III). However, decomposition of this intermediate can proceed by several routes. Not only could loss of configuration occur in the solvolysis of the organometallic

(13) This selectivity might be the result of a difference in hybridization of the attacking reagent. The structure of both acetate salts have not been examined, but thallium triacetate in simplest terms can be represented as a planar molecule with sp^2 bonds to the acetate groups. An empty p-orbital can function as a Lewis acid and effectively overlap with the electrons in the cyclopropane bond. Lead tetraacetate is probably tetrahedral and would have to either ionize or expand its valence shell in order to react with the cyclopropane bond. The selectivity of thallium triacetate might be a reflection of the available p-orbital, and therefore, mercury salts might also be selective cleavage reagents.

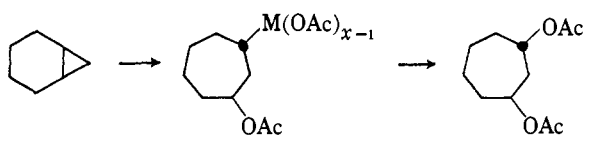
(14) The absence of unsaturated compounds derived from intermediate I may be either a reflection of the S_N2 character of solvolysis of primary organometallic derivatives or participation of the acetate group on the ring leading to substitution rather than elimination of a proton to yield an exocyclic double bond. The known high carbonium ion character developed in solvolysis of organomercury compounds make the latter alternative more likely.

derivative, but unsaturated products would also be expected. A high proportion of unsaturated monoacetates consisting of Δ^2-cycloheptenyl acetate (IV) and Δ^3-cycloheptenyl acetate (V) is observed. There appears to be little significant difference between the two possible hydrogens that could be eliminated. The yields of both isomers are comparable with lead tetraacetate. However, with thallium triacetate, only the Δ^3-cycloheptenyl acetate is obtained. This difference in the unsaturated component of the reaction mixture may be significant feature in distinguishing the decomposition route for organometallic compounds.[15]



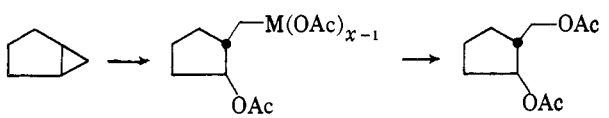
III IV V

The diacetate resulting from the solvolysis of the seven-membered ring organometallic compound could either be *cis* or *trans* as a center determining stereochemistry is involved in the decomposition step. Decomposition of a secondary organometallic derivative would be expected to proceed with loss of stereochemistry in the absence of any group participation.[16] If a SN2 pathway is operative then *cis*-1,3-diacetoxycycloheptane should be observed. Since neither of these two predictions is in agreement with the experimental observation of *trans*-1,3-diacetoxycycloheptane (VI) formation, it is probable that the geometry of the cycloheptane system allows 1,3-acetoxy participation which preserves the stereochemistry of the cleavage product.



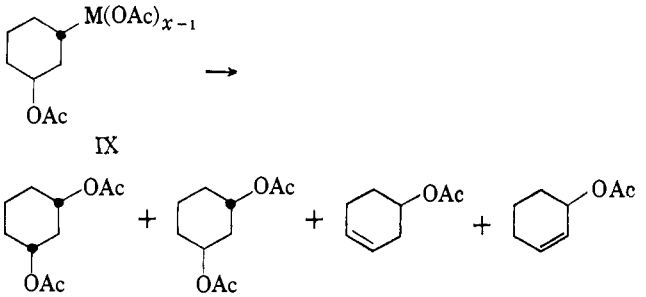
III VI

The cleavage of the external bond of bicyclo[3.1.0]hexane proceeds to yield exclusively *trans*-2-acetoxymethylcyclopentyl acetate (VIII). This product is undoubtedly formed by a stereospecific *trans* addition of either lead tetraacetate or thallium triacetate to yield organometallic derivatives (VII) whose stereochemistry is unaffected in the decomposition step.



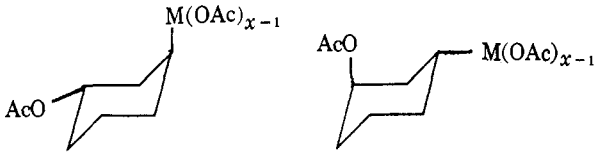
VII VIII

The secondary organometallic derivative IX formed by internal bond cleavage of bicyclo[3.1.0]hexane yields unsaturated material and mixture of isomeric diacetates. Both *cis*- and *trans*-1,3-diacetoxycyclohexane are observed. However, with lead tetraacetate, the *cis* isomer is formed in the larger amount. The



IX

predominance of the *cis* isomer could be accounted for by maintaining the *trans* addition mechanism and considering the conformer IXa and IXb of the intermediate organometallic derivative. The relative amounts of *cis* and *trans* diacetates and olefins is a function of the populations of the two conformations and their relative rates of decomposition. Since the conformational preferences of the triacetoxy lead and diacetoxy thallium groups are not known and the relative rates of solvolysis of each conformer cannot be estimated unambiguously, discussion of this problem will be postponed until model organometallic derivatives of fixed stereochemistry can be examined.



IXa IXb

Bicyclo[2.1.0]pentane is cleaved exclusively at the internal bond with both lead tetraacetate and thallium triacetate. The stereochemistry of the lead tetraacetate cleavage product reported by Criegee[6a] for the 1,3-diacetoxycyclopentane was *cis*. However, assignment of stereochemistry was dependent on the corresponding diols which were assigned by Owen and Smith.[17] The assignment of the diols was ultimately dependent on the stereochemistry of the isomeric 3,5-dibromocyclopentenes which were assigned by Thiele.[18] Winstein[19] reversed the assignment of Thiele slightly before the report of Criegee and this change unfortunately must have been overlooked. We have repeated Criegee's work and the stereochemistry of the diacetate is *trans* as anticipated. The isolated yields of the diacetate and an unknown lower molecular weight material reported by Criegee were 15 and 20%, respectively. The ratio of the isolated yields are in fair agreement with our v.p.c. analysis. No *cis*-1,3-diacetoxycyclopentane was observed by v.p.c. The unidentified material reported by Criegee is a mixture of Δ^2-cyclopentenyl acetate and Δ^3-cyclopentenyl acetate. The most rational way of explaining the observed products is to maintain the *trans* addition mechanism. Solvolysis of the intermediate organometallic derivative must occur with net retention of stereochemistry as a result of 1,3-acetoxy participation.

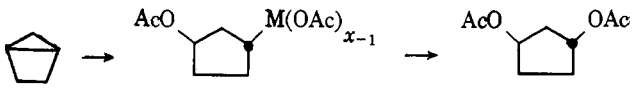
(15) The decomposition of the organothallium intermediate may proceed to a large degree *via* a conformation in which the acetoxy group can assist in the departure of the metallic species. If this occurs then the transition state resembles a bicyclic skeleton of the [4.3.1] variety, and the incipient double bond would prefer to develop in the larger ring, which would yield the Δ^3-cycloheptenyl acetate. In the organolead intermediate a more energetic carbonium ion might be formed which would lead to less discrimination in the choice of the two possible protons to be ejected.

(16) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **85**, 363 (1963).

(17) L. N. Owen and O. N. Smith, Jr., *J. Chem. Soc.*, 4055 (1952).

(18) J. Thiele, *Ann.*, **314**, 300 (1900).

(19) W. G. Young and S. Winstein, *J. Am. Chem. Soc.*, **78**, 4338 (1956).



Winstein[20] has observed that acetate participation occurs in the reaction of thallium triacetate with cyclohexene to give net retention of stereochemistry in the absence of water.

Moon[6g] reported that the acetate esters of *endo*- and *exo*-bicyclo[3.1.0]hexanol are formed in nearly equimolar amounts in the cleavage of bicyclo[3.1.0]hexane. In our work at 75° which is 43° lower than the conditions employed by Moon, these products were not observed. The observed isomeric acetate esters of bicyclo[3.1.0]hexanol might result from an α-acetoxylation mechanism similar to that observed for allyl and benzyl systems. This process would certainly become competitive at the temperature of refluxing acetic acid. Moreover, higher selectivity ratios for the cleavage reaction of bicyclo[4.1.0]heptane are noted in our work, and significantly lower quantities of olefinic material resulting from the internal cleavage are obtained. However, the reactivity of the cyclopropanes is such that considerably lower temperatures than those employed by Moon can be used. The chemistry of lead tetraacetate is plagued by the changes in mechanism of reaction by subtle changes in reaction conditions. This question of mechanistic changeover is currently being investigated. Moreover, a kinetic investigation of the cyclopropane cleavage reaction is being initiated.

A comparison of the mercuric acetate cleavage reaction reported by Levina is difficult as the reported experimental indicates the unquantitative nature of the experiments. Levina observed exclusive external bond cleavage in bicyclo[4.1.0]heptane and reported a 86% yield. The cleavage of bicyclo[3.1.0]hexane occurs exclusively at the external bond but only a 60% yield is obtained. The internal bond cleavage product is secondary and would be expected to solvolyze approximately 10^5 times faster than the primary product resulting from external bond cleavage[10] and therefore the exclusive external cleavage is probably the result of the decomposition of one isomer.

Experimental

All of the authentic samples utilized for comparison of the cleavage products except *cis*- and *trans*-2-acetoxymethylcyclopentyl acetate were prepared by methods described in the references given in Tables I, II, and III, of the section entitled Results.

cis- and trans-2-Acetoxymethylcyclopentyl Acetate. A solution of 10.0 g. (0.058 mole) of cyclopentan-2-one-carboxylic acid in 50 ml. of ethanol was dropped into a solution of 1.8 g. (0.033 mole) of potassium borohydride in 100 ml. of ethanol. After stirring for 5 hr., the solvent was removed by distillation and the organic residue was dissolved in ether. The ether was removed by distillation and the product was analyzed by v.p.c. Two products in the ratio of 4:1 were observed. The major product had the shorter retention time on a 20% Degs on Chromosorb column. Fractionation of the reaction products yielded a major fraction boiling at 92° (3 mm.). A minor fraction boiling at 104° (3 mm.) was also obtained. The major fraction was assigned the *cis* configuration by virtue of its lower boiling point, retention time on polar columns, and the known direction of borohydride reduction. A standard lithium aluminum hydride reduction of both isomers followed by acetylation utilizing acetyl chloride and pyridine in ether yielded the two isomeric 2-acetoxymethylcyclopentyl acetates. The acetates were collected by v.p.c. and their structures were confirmed by n.m.r. as described in the Results section. The methylene hydrogens on the carbon bearing the acetoxy group are nonequivalent in the *cis* isomer giving rise to an eight-line multiplet whereas in the *trans* isomer the methylene hydrogens are nearly equivalent.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: (*cis*) C, 59.95; H, 8.01; (*trans*) C, 59.96; H, 7.96.

Cleavage of Bicyclo[n.1.0]alkanes. The cleavage of bicyclo[*n*.1.0]alkanes is described for the reaction of bicyclo[4.1.0]heptane with lead tetraacetate. The cleavage of the other compounds utilized in this study was similar except for temperature and reaction time. Bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane were cleaved at 75° whereas bicyclo[2.1.0]pentane was cleaved at 25°. The reaction times for the lead tetraacetate cleavages were 60, 26, and 24 hr. for the [4.1.0], [3.1.0], and [2.1.0] systems, respectively. The corresponding times for thallium triacetate cleavage were 82, 62, and 60 hr. A mixture of 1.0 g. (0.01 mole) of bicyclo[4.1.0]heptane and 2.0 g. (0.0046 mole) of recrystallized lead tetraacetate was placed in 10 ml. of anhydrous acetic acid in a sealed flask. The reaction vessel was placed in a 75° constant-temperature bath for 60 hr. After sufficient time for reaction had occurred, 20 ml. of ice-cold water was added. The mixture was extracted with three 20-ml. portions of ether and the combined ether extracts were washed twice with water, three times with sodium bicarbonate, and finally with water. The ether solution was dried over magnesium sulfate and analyzed by v.p.c. The solvent was then removed by distillation and the products were collected by v.p.c. for n.m.r. analysis. Crude reaction mixtures were examined by n.m.r. prior to v.p.c. analysis to ensure that complications due to selective destruction of reaction components did not occur.

(20) C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963).